

SI2108: Traceable calibration of Hydrogen Chloride (HCl)

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Abstract

In this white paper, we discuss the calibration of Hydrogen Chloride in Picarro’s Cavity Ring Down Spectrometers.

History

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Contents

Abstract	1
History	1
Spectroscopy	2
Original Calibration of HCl at Picarro	2
Validation of the HCl Calibration	2
HITRAN Spectral Database	2
Gravimetrically prepared cylinders	3
Method for Calibration of Individual Instruments	6
Stability of the Calibration Over Time	9
Summary	10

Spectroscopy

Hydrogen Chloride (HCl) is measured in the near infrared region of the spectrum. Figure 1 shows the spectral region that the instrument uses to quantify HCl, H₂O, and CH₄. The CRDS instrument rapidly (in about 2-5 seconds) scans this spectral region using a narrowly tunable Distributed Feed Back (DFB) fiber-coupled laser. The resulting spectrograms are analyzed using a non-linear least squares optimization algorithm, using pre-calculated model functions for each of the spectral features in this region. The concentrations of HCl, H₂O, and CH₄ are reported by the instrument on the user interfaces and the data logs.

Original Calibration of HCl at Picarro

In 2015, Picarro measured the calibration factor of an early HCl instrument operating at a cavity temperature of 45 C, using a gravimetrically prepared gas bottle¹. In 2016, Picarro elected to increase the cavity temperature to 80 C, which led to a significant improvement in the response time due to reduced retention on the wetted surfaces of the instrument. Because Picarro instruments include careful measurements of the temperature and pressure of the gas, and because ringdown is an absolute measurement of the total loss in the optical cavity, the instrument-to-instrument repeatability is typically about 1%. For this reason, and because reactive gases are extremely hard to calibrate to better than 5-10% accuracy, we have elected to retain the original 2015 calibration factor. The 45 C calibration factor was rescaled by considering the change in the number density in the cavity as well as changes in the absorption cross section due to ground state population redistribution when going from 45 to 80 C. This change was then applied as a ratio to the original 45 C calibration factor, resulting in a final calibration factor of 0.352 ppb HCl per ppb / cm × wavenumber².

Validation of the HCl Calibration

HITRAN Spectral Database

We have validated the absolute HCl calibration using two methods. In the first method, we have used the HITRAN database (Rothman et al. 2012³) to directly calculate the absorption of the HCl spectral line employed in the Picarro HCl instrumentation. Using the intensity value, ground state energy, and

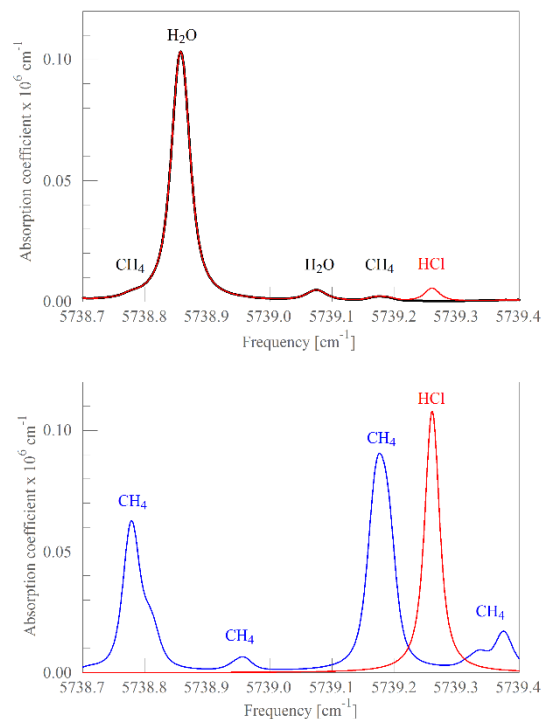


Figure 1: HCl spectral region, showing major features for H₂O and CH₄. The instrument reports all three species. CH₄ can be used as a 'proxy' for the calibration and proper operation of the instrument.

¹ HCl in balance air (Cyl #: AT021232, Matheson Gas, Basking Ridge, NJ), certified concentration 9.83 ppm, accuracy ± 10%.

² Unlike the HF and NH₃ analyzers, which use absorption peak height (in units of ppb / cm) to compute the concentration in the CRDS cavity, the HCl analyzer uses absorption peak area (in units of ppb / cm × wavenumbers). The difference has no consequence on the ultimate operation and performance of the analyzers.

³ Rothman, Laurence S., et al. "The HITRAN2012 molecular spectroscopic database." *Journal of Quantitative Spectroscopy and Radiative Transfer* 130 (2013): 4-50.

partition function from HITRAN, and our measured line shape parameters to relate integrated absorption to peak absorption, we arrive at a calibration factor 0.309 ppb HCl per ppb / cm × wavenumber, which is 12% smaller than the 0.352 calibration based on the gravimetrically prepared cylinder measurement.

Gravimetrically prepared cylinder

In the second method of validation, we have obtained a gravimetrically prepared standard of HCl in a specially coated cylinder from AirGas, Inc. This standard was prepared with a concentration of about 4 ppm. Because we want to calibrate the instrument in the relevant operating range of 0 – 50 ppb, we performed a dilution experiment. The setup for this dilution experiment is shown in the figure below. All the experiments in this section were performed on a single instrument (S/N: SADS2004), which we have designated as our ‘Golden’ HCl analyzer. We will describe how this Golden analyzer is used in more detail in later sections.

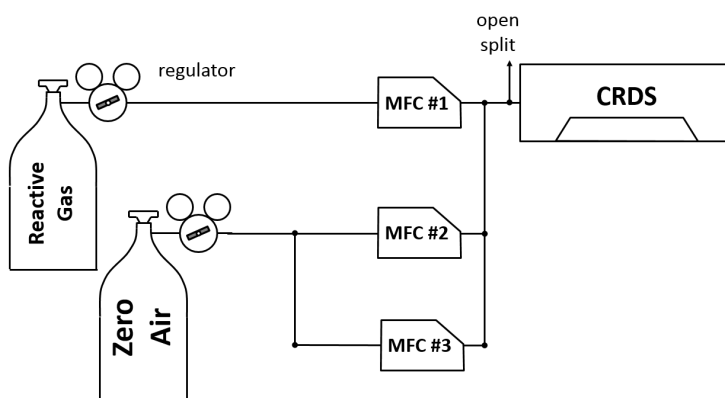


Figure 2: Schematic for performing Dilution Experiment #1. PFA tubing was used throughout, and the regulator on the reactive gas cylinder was Silconert-coated for improved performance.

Calibrated mass flow controllers (MFCs)⁴ were used to prepare the gas mixtures. The total flow from the dilution system always exceeded the ~2 slm flow through the instrument, with the excess gas directed to ambient via the open split. The reactive gas concentration as prepared by the dilution system is given by the following expression:

$$c_{reactive} = \frac{f_1}{f_2 + f_3} c_{cylinder}$$

We ran the dilution system with four separate settings for $f_1 = 2.0, 6.5, 15,$ and 32 sccm; for each setting of f_1 , $f_2 = 500$ sccm, and $f_3 = 2, 3, 4, 5,$ and 6 slm, with steps 400 seconds long. The rated cylinder value is 5.16 ppm. We ensured that the concentration delivered by the system was stable prior to beginning the measurements. The time series measured using these settings is shown in Figure 3.

⁴ MFCs (MCS-50SCCM-D, MC-500SCCM-D, MC-10SLPM-D; Alicat, Inc, Tucson, AZ). The accuracy of the MFCs used in this experiment is ±0.8% of reading +0.2% of full scale.

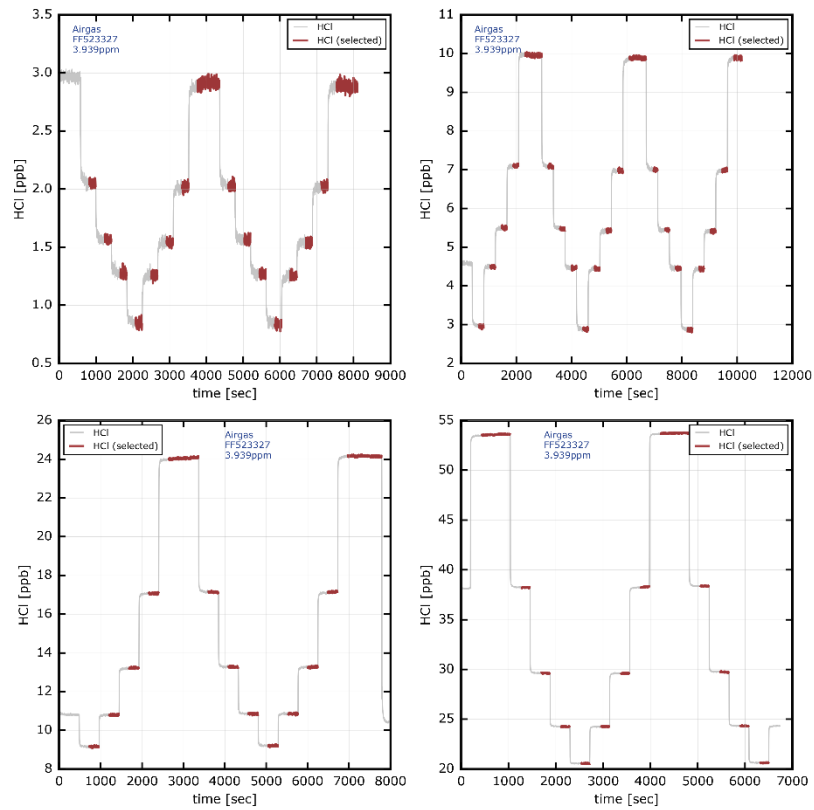


Figure 3: time series with f_1 set to 2.0, 6.5, 15.0, and 32.0 sccm (upper left, upper right, lower left, and lower right panels, respectively).

We can then plot the measured concentration vs. the expected concentration from this dilution system (given the assigned value of the cylinder and the set flow rates through the MFCs). Figure 5 shows these data, along with a 1:1 line for reference.

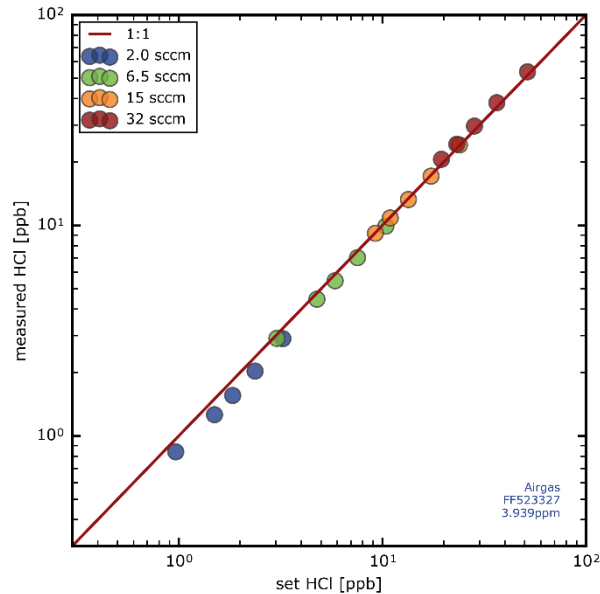


Figure 4: Measured HCl signal as a function of the expected value, for different values of f_1 .

It appears from this figure that the slope of the calibration curve depends upon the flow through MFC #1. This can be seen more clearly when plotting the ratio of the measured signal to the expected signal for the two data sets, as is shown in Fig. 6.

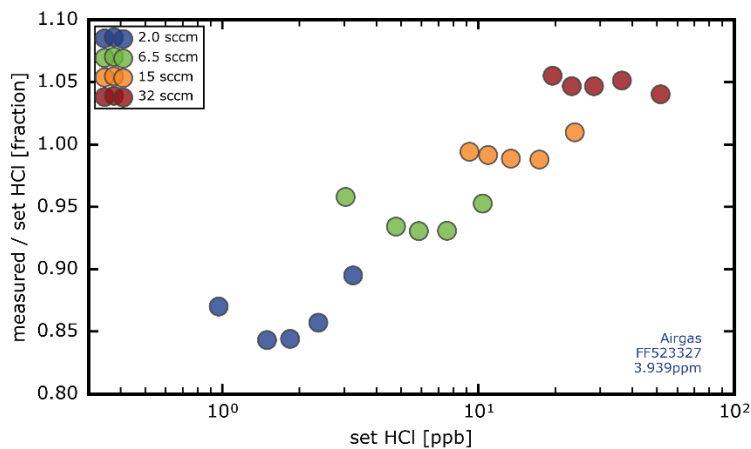


Figure 5: ratio of the measured HCl signal to the set point, for different values of f_1 .

Looking at Fig. 6, we note that for a given flow through MFC #1, the ratio of the measurement to the setpoint is relatively constant, indicating that the instrument responds linearly to the measurement. This is especially clear where data from adjacent flow settings overlap (e.g., ~ 10 ppb), indicating that instrument linearity is not the cause of the error. We may also reject the hypothesis of a flow error in the reactive gas MFC; we tested the dilution with a non-reactive gas (methane) and found that the dilution system works as expected given the specifications of the MFCs. We therefore conclude that some of the HCl is being lost due to reactivity in the dilution system, and that at lower flows, some of the HCl is lost due to reactivity of the wetted surfaces of the delivery system. MFC #1 itself is a likely

candidate, because the wetted surfaces have not been passivated with Silconert. If we extrapolate these results to even higher flows, we see that the calibration slope as derived from these dilution experiments is about 1.1 to perhaps 1.2 times the default calibration slope.

From these validation experiments using gravimetrically prepared standards, we draw the following conclusions:

1. For HCl, the choice of wetted materials and flows can affect the overall delivery of the reactive gas to the instrument.
2. The calibration slope *increases* with *increasing* flow through the reactive gas delivery system, from which we infer that one or more materials in the system is reacting with the HCl and reducing the total amount of HCl delivered to the instrument.

We summarize the HCl calibration slope measurement of the ‘Golden’ HCl instrument below:

Method	Relative Slope
2015 Direct Cylinder Calibration	1.0
2012 HITRAN	0.88
Cylinder Dilution Experiment	1.1 – 1.2

Final Conclusion: We have decided to retain the calibration constant as defined by the 2015 Direct Cylinder Calibration; i.e., a calibration constant of 0.352 ppb HCl per ppb/cm x wavenumber. This calibration factor will be applied to all SI2108 instruments.

Method for Calibration of Individual Instruments

Because it is difficult to prepare and deliver a constant and known concentration of HCl, individual instrument calibration becomes a challenge. The desire to have all instruments measuring the same value further complicates the situation. We have therefore selected the following calibration approach:

1. Carefully calibrate a “Golden” instrument.
2. Use this Golden instrument as a transfer standard to cross-calibrate each instrument built at the factory. Using the Golden instrument as the calibration reference, rather than the gas preparation system, means that the stability and repeatability requirements for sample preparation can be relaxed dramatically.
3. Ensure the calibration of the Golden instrument over time by checking the calibration of this instrument with a non-reactive proxy gas. In the case of HCl, this proxy gas is CH₄.

The apparatus used for performing the cross-calibration experiment is shown below. The flows through the MFCs are set to produce a set of concentration challenges to both instruments simultaneously. Because the two instruments share a single gas preparation system, losses of HCl in this system do not affect the ultimate calibration of the Device Under Test (DUT).

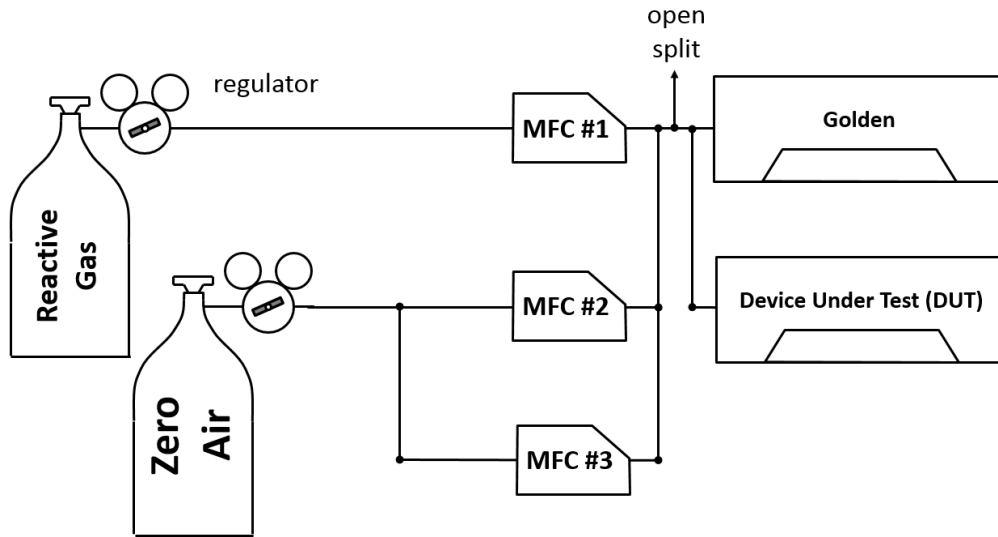


Figure 6: Cross-calibration setup used to transfer the calibration of the Golden instrument onto the DUT.

For a typical dilution profile, we keep MFC #2 and MFC #3 at a constant flow of 500 sccm and 2 slm, respectively, and step MFC #1 from 1 to about 20 sccm and back down, over a period of several hours. This pattern is generally repeated twice. A typical time series is shown below.

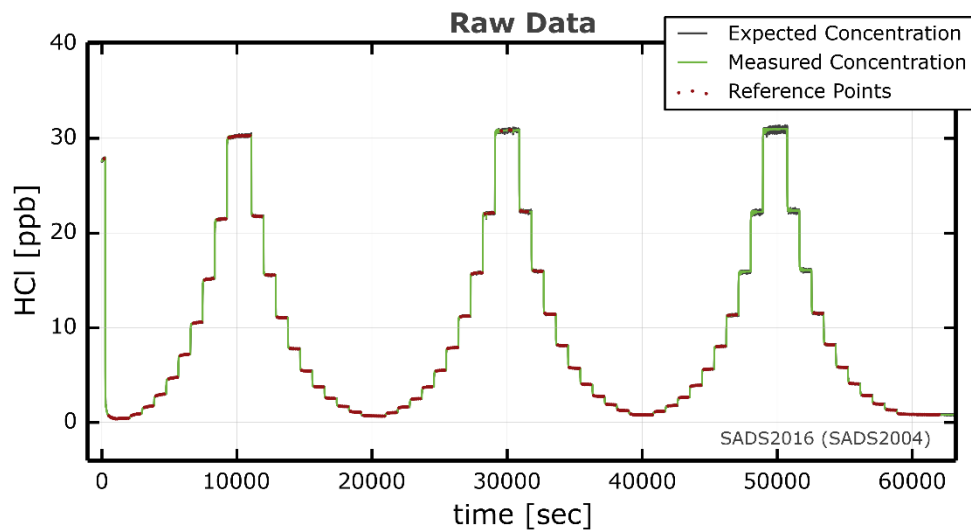


Figure 7: Time series for the Golden Instrument (SADS2004, in gray) and the DUT (SADS2016, in green). The reference points (shown in red) are selected from both time series to meet minimum criteria for stability. These points are used in further analysis.

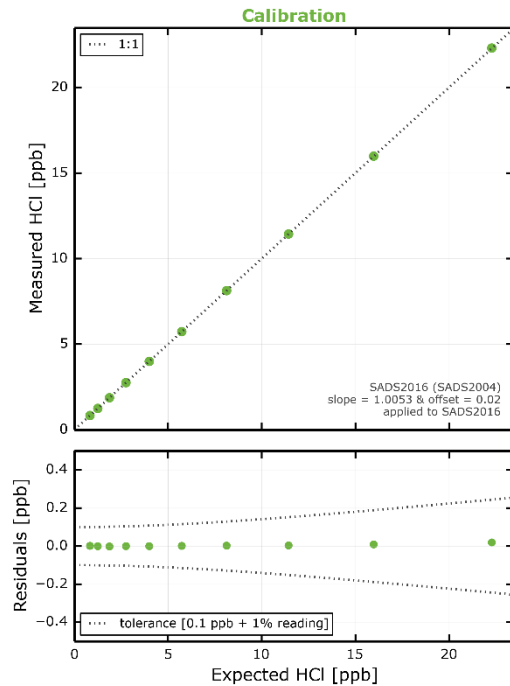


Figure 8: Calibration data derived from Fig. 7.

Note that it is not necessary to assume that the concentration delivered by the dilution system is determined by the concentrations in the bottles and the flows through the MFCs – the Golden instrument provides traceability to the DUT. From these data we can determine the calibration of the instrument, by plotting the DUT measurements as a function of the Golden instrument values. These calibration data are shown in Fig. 8. To create this figure, we determine the slope (1.0053 ppb / ppb) and offset (0.02 ppb) from the first cycle of data, and then we apply that slope and offset to the second cycle of data. This second cycle of data are plotted in Fig. 8.

It is important to note that this slope and offset are **not** applied to the DUT instrument calibration itself; the DUT retains the default calibration of 0.352 ppb per ppb/cm × wavenumber that is applied to all instruments, for the following reasons:

1. The response time of the two instruments is not identical, which can lead to small but measurable differences in the signals observed on the two instruments as the concentration system, even though they share an inlet and sample preparation system. These differences can distort the calibration curve.
2. Because HCl is retained on the wetted surfaces of the instruments, sometimes for hours or more, the fact that each instrument may have been exposed to differing amounts of HCl can also distort the calibration curve.

We do apply a pass / fail check on the calibration curve: the calibration slope must be within 5% of 1.0 (i.e., $0.95 \leq \text{slope} \leq 1.05$). If the test passes this criterion, then the standard calibration constant of 0.352 ppb per ppb/cm × wavenumber is retained; if the test fails, we investigate the failure and rework the instrument. In addition, the residuals of the calibration curve must lie within the gray dotted lines on the lower panel of Fig. 8.

From this second set of data, we also derive the linearity of the instrument⁵, which is defined as the ratio of the maximum excursion of the residual from a linear fit to the total span of concentration. Figure 17 shows this linearity plot; the gray dotted lines in the lower figure indicate the requirement of 1% for the linearity.

Finally, from each cycle, we can determine the Method Detection Limit (MDL)⁶. The MDL data are shown in Fig. 18. The MDL must be lower than 0.5 ppb on both cycles for the

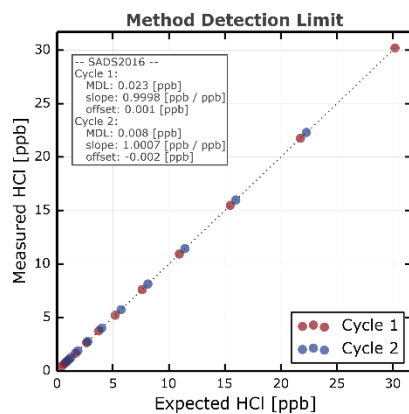


Figure 9: MDL plot

instrument to pass the test.

Stability of the Calibration Over Time

It is important to be

assured that the calibration of each individual instrument will be stable between calibration verification events, which may occur as frequently as once per year, or even more seldom. It is very difficult to keep HCl standards stable for long periods of time. For example, permeation tubes and gravimetrically prepared cylinders

of HCl generally have a certified life of no more than 6 months. We therefore have little direct evidence of the stability of our HCl instruments over time. There exists however ample evidence of the stability of the calibration of CRDS spectrometers over time periods of months and years. In Yver-Kwok et al. (2015)⁷, 47 Picarro CRDS instruments that measure CO₂, CH₄, and CO were studied, including 15 CRDS instruments that were calibrated in the field using highly accurate greenhouse gas standards. It was found that the calibration slope drifts typically about 0.1% / year; the largest drift observed overall was 0.3%. Because the CRDS spectrometers in these greenhouse gas instruments are functionally identical to the spectrometers used to quantify HCl⁸, we may then conclude that the HCl calibration slope in the SI2108 should exhibit a similar level of stability (<0.5%) over life. Because we expect the instrument stability to exceed our ability to deliver a known concentration of HCl, we recommend a yearly calibration validation, using either the reactive gas HCl itself, or, more simply, the non-reactive proxy gas

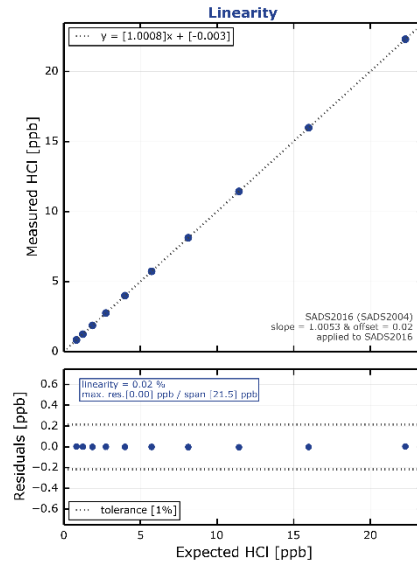


Figure 10: Linearity plot.

⁵ IEC 61207-1

⁶ SEMI C10-1109

⁷ Yver Kwok, C., Laurent, O., Guemri, A., Philippon, C., Wastine, B., Rella, C. W., Vuillemin, C., Truong, F., Delmotte, M., Kazan, V., Darding, M., Lebègue, B., Kaiser, C., Xueref-Rémy, I., and Ramonet, M.: Comprehensive laboratory and field testing of cavity ring-down spectroscopy analyzers measuring H₂O, CO₂, CH₄ and CO, Atmos. Meas. Tech., 8, 3867-3892, doi:10.5194/amt-8-3867-2015, 2015.

⁸ The key exception is that the target wavelength as determined by the near-infrared spectra of the molecules is different. However, the pressure and temperature sensing and control systems, the wavelength monitor, the laser technology, the ring down cavity design, the electronics, and the firmware & software are all the same.

CH₄. There is no need to perform a true calibration in which the calibration slope is changed per the results of a direct HCl calibration experiment.

Summary

For all Picarro HCl instruments (SI2108):

1. The calibration factor relating the optical absorbance in the measurement cell to the concentration of HCl is the same value for all instruments: 0.352 ppb HCl per ppb/cm × wavenumbers.
2. This calibration factor, derived from a gravimetrically prepared cylinder, has been validated against the 2012 HITRAN spectroscopic database and against a second gravimetrically prepared cylinder standard that was diluted using calibrated mass flow controllers.
3. The proper calibration of all instruments is verified at the factory using a Golden instrument. The stability of the Golden instrument will be verified periodically (about once / year), using both reactive HCl and a non-reactive proxy gas, CH₄.
4. While in the field, the calibration of the instrument can be verified using a direct HCl calibration experiment, or, more simply, by testing with CH₄.